

# **Grand canonical molecular dynamics for water and methanol systems<sup>1</sup>**

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## ABSTRACT

An algorithm was developed enabling implementation of Nosé-Hoover thermostat within the framework of grand canonical molecular dynamics. The proposed algorithm could readily be extended to mixtures of molecular species with different chemical potentials as shown in the paper. This algorithm was first applied to simulate an  $\mu$ VT ensemble of TIP4P water molecules at 298 K by means of a system comprising a number of full particles and a single scaled (fractional) particle, with the scaling factor considered a dynamic variable in its own right and chemical potential a preset parameter. Our finding showed that the scheme with a single fractional particle tended to freeze in metastable states as well as failed to reproduce either real-life or model-specific chemical potential of water. In order to overcome this inadequacy the treatment of Pettitt and co-workers was extended to introduce multiple fractional particles. The extended scheme was able to reproduce the actual density of water for the driving chemical potential of  $-24.0$  kJ/mol, as well that of methanol for  $-19.0$  kJ/mol. The actual behaviour of density as a function of chemical potential also agreed quite well with both the results of thermodynamic integration and the findings of Pettitt and co-workers.

KEY WORDS: chemical potential; grand canonical molecular dynamics; methanol; TIP4P water

## 1. INTRODUCTION

It would be hard (if not impossible) to overestimate the importance of chemical potential, free energy, and other entropy-related thermodynamic functions when dealing with phase or chemical equilibria, as well as nonequilibrium dynamics (particularly diffusion in multicomponent systems). It is the spatial distribution of excess chemical potential which ultimately governs the transport of solutes across biological bilayers [1], permeation of gas mixtures through carbon and silicate membranes [2,3], gas flow in slit-shaped micropores [4], and other interfacial phenomena.

But unlike potential energy, pressure, temperature and various correlation functions which can readily be expressed as ensemble averages of pairwise additive functions, the calculation of chemical potential and other ‘thermal’ properties requires the estimate of a high dimensional integral. Decades of research effort have yielded several techniques suitable for computation of chemical potential and free energy. Thermodynamic integration, the simplest and the most reliable of these techniques, requires several simulations to obtain entropy-related properties of interest. Straightforward application of Widom’s particle insertion method [5,6] is known to fail at high densities due to poor sampling. Various versions of cavity-biased insertion technique were used by several authors to overcome the sampling problem for water and other dense liquids [1,7,8].

Or alternatively, chemical potential could be treated as a controlled variable with the number of molecules becoming a dynamic variable. Depending on the starting N-constant system the ‘conjugate’ one can take the form of either grand canonical ( $\mu VT$ ) or  $\mu PT$  ensemble.

## **2. SYSTEMS DRIVEN BY CHEMICAL POTENTIAL GRADIENT: APPROACHES AND SIMULATION SETUPS**

Earlier simulations of flux in slit pores and diffusion of gas through micro- and nanopore membranes [2,3,4,9] used the recipes of grand canonical Monte Carlo to control the chemical potential in two control volumes. Their hybrid GCMC-molecular dynamics (GCMC/MD) scheme employed two types of moves: stochastic MC moves which aimed to adjust the density in control volumes, and dynamic ones providing the mass transport across the system. Typical hybrid Monte Carlo-molecular dynamics approaches suffer from two drawbacks. First, they call for insertion of a fully-fledged molecule, and the acceptance probability of such a step will be quite low for dense fluids (as witnessed by poor sampling of Widom's particle insertion which makes it fail in case of water) thus increasing drastically the number of necessary attempts. Second, and the most important, disadvantage lies in the fact that if the insertion step is accepted, the newly created particle is assigned a velocity drawn from Maxwell's distribution. In one of the references [4] the particle was also assigned a streaming velocity calculated from averaged previous flux, which raises the problem of self-consistency. Given the relatively small size of control volumes and the possibility of several particles being created or deleted within just a few time steps, there are no guarantees against GCMC/MD procedure completely destroying the dynamics of the system and thus defeating the purpose of the exercise - simulating mass transport driven by the gradient in chemical potential. In case of the pure grand canonical MD the newly created almost-zero particle is assigned zero velocity, the system is undisturbed, and the fledgling particle is free to probe its surrounding and gain appropriate velocity. Playing the devil's

advocate we must point out that the advantage of the MC scheme lies in the fact that while any straightforward application of grand canonical MD relies on the ensemble's intrinsic responses to correct the possible density deviation in the control volumes, the hybrid GCMC/MD technique allows to tailor the ratio between stochastic and dynamic steps to match the system's dynamics.

Application of the relationship between density and chemical potential allows using both GCMC/MD and GCMD to calculate chemical potential in model single-component systems of interest (*e. g.* [11,12]). The application of the schemes to interface systems could follow the general setup suggested in [3,9]. One possible way to overcome the problem of slow response of pure GCMD mentioned earlier will be to take a leaf out of hybrid technique' book and periodically freeze the entire system outside the control volumes (the distance between them insures that they don't affect each other). While the GCMD steps are executed in two control volumes, the rest of the system is treated as static background. Full and fractional particles alike are confined to control volumes. In between the grand canonical steps it is the number dynamics that will be put on hold, with the fractional particles bouncing from the control volume walls in z-direction.

### **3. GRAND CANONICAL MOLECULAR DYNAMICS: GENERAL SCHEME AND IMPLEMENTATIONS**

Grand canonical MD proposed in a series of papers by Pettitt and co-authors (see 11,12,13 and references therein) is implemented by introducing an additional dynamic variable, the number of particles. At any given moment, this number could be written as  $N+\zeta$ , where  $N$  is integer and stands for full particles, while  $\zeta$  determines the degree of

presence of a fractional particle. Following Pettitt, we have defined  $\zeta$  as a coefficient used both to scale linearly the interaction between the fractional particle and the full particles, as well as its contribution to the system's kinetic energy. It could be shown [10,11,12] that both scalings give rise to additional terms in the open system Hamiltonian and equations of motion. In [13] a version of the grand canonical molecular dynamics was used to implement a Gibbs ensemble for truncated and shifted Lennard-Jones fluid. The Gibbs ensemble specifics imply additional constraints on the fractional particle dynamics (fractional particles in two different phases must add up to unity) as well as presence of additional volumes-dependent terms in the equations. Still, provided the asymmetric starting densities in the two compartments, the Gibbs ensemble molecular dynamics algorithm successfully reproduced the results obtained using Gibbs ensemble Monte Carlo simulation [13].

The Hoover formulation of Nosé-Hoover thermostat [14,15] was implemented where one starts from a set of coupled equations of motion rather than a Hamiltonian:

$$m_{a(i)} \frac{d\mathbf{v}_i}{dt} = \mathbf{F}_i - \eta_{ir} m_{a(i)} \mathbf{v}_i \quad (1)$$

$$\mathbf{F}_i = -\sum_{i \neq j} \frac{\partial U_{ij}}{\partial \mathbf{x}_j} - \sum_a \sum_{f_a} \zeta_{f_a} \frac{\partial U_{if_a}}{\partial \mathbf{x}_{f_a}} \quad (2)$$

$$m_a \frac{d(\zeta_{f_a} \mathbf{v}_{f_a})}{dt} = \mathbf{F}_{f_a} - \zeta_{f_a} \eta_{ir} m \mathbf{v}_{f_a} \quad (3)$$

$$\mathbf{F}_{f_a} = -\zeta_{f_a} \sum_i \frac{\partial U_{if_a}}{\partial \mathbf{x}_{f_a}} - \zeta_{f_a} \sum_{f \neq f_a} \zeta_{f_b} \frac{\partial U_{ff_a}}{\partial \mathbf{x}_{f_a}} \quad (4)$$

$$\frac{d\eta_{tr}}{dt} = \left[ \sum m \mathbf{v}_i^2 + \sum_a \zeta_{f_a} \mathbf{v}_{f_a}^2 - X_{tr} k T_{tr} \right] / Q_{tr} \quad (5)$$

$$\frac{d\eta_{rot}}{dt} = \left[ \sum \mathbf{j}_i \mathbf{w}_i + \sum_a \zeta_{f_a} \mathbf{j}_{f_a} \mathbf{w}_{f_a} - X_{rot} k T_{rot} \right] / Q_{rot} \quad (6)$$

$$\frac{d\mathbf{j}_i}{dt} = \mathbf{t}_i - \eta_{rot} \mathbf{j}_i \quad (7)$$

$$\mathbf{t}_i = - \sum_{i \neq j} \frac{\partial U_{ij}}{\partial \mathbf{x}_j} \times \mathbf{x}_j - \zeta_f \frac{\partial U_{if}}{\partial \mathbf{x}_f} \times \mathbf{x}_f \quad (8)$$

$$\frac{d(\zeta_f \mathbf{j}_f)}{dt} = \mathbf{t}_f - \zeta_f \mathbf{j}_f \quad (9)$$

$$\mathbf{t}_f = - \zeta_f \sum_i \frac{\partial U_{if}}{\partial \mathbf{x}_f} \times \mathbf{x}_f \quad (10)$$

$$\frac{d\mathbf{q}}{dt} = \mathbf{Q} \mathbf{w} \quad (11)$$

$$\mathbf{W}_a \frac{d^2 \zeta_{f_a}}{dt^2} = \frac{1}{2} m_a \mathbf{v}_{f_a}^2 - \sum_{i \neq f_a} U_{if_a} - \frac{3}{2} k_B T \frac{1}{\zeta_{f_a}} + \mu_a^{ex} \quad (12)$$

Above equations have been extended to a mixture of different molecules and several fractional particles (subscript  $f$ ), with subscript  $a$  indicating the molecular species;  $\mathbf{x}$  - COM coordinates;  $U$  - unscaled potential interaction;  $m\mathbf{v}$  - unscaled translational momenta;  $\mathbf{j}$  - unscaled angular momenta;  $\mathbf{F}$  - scaled forces;  $\mathbf{t}$  - scaled torques;  $\mathbf{I}$  - moment of inertia tensor;  $\mathbf{w}$  - angular velocity related to angular momentum by  $\mathbf{w} = \mathbf{I}^{-1} \mathbf{j}$ ;  $\mathbf{\hat{w}}$  - transposed body-centred angular velocity augmented by a zero to form a four-component vector;  $\mathbf{q} = [q_0, q_1, q_2, q_3]^T$  - four-component quaternion representing the

orientation of the molecule [16];  $\mathbf{Q}$  - matrix (6c) of [17];  $T_{tr}$  and  $T_{rot}$  - required translational and rotational temperatures;  $\eta_{tr}$  and  $\eta_{rot}$  - translational and rotational friction parameters of Hoover formulation [15],  $X_{tr}$  and  $X_{rot}$  - number of respective degrees of freedom,  $Q_{tr}$  and  $Q_{rot}$  - thermostat masses determining response times;  $W$  is an adjustable masslike parameter similar to thermostat masses (ranging in hundreds of  $\text{kJ ps}^2/\text{mol}$  in our case),  $\mu_{ex}$  - excess chemical potential.

Ref. [10-12] used pure Nosé thermostating that necessitates some sort of RATTLE algorithm to handle the holonomic constraints. Our application of quarternion scheme requires us to control two loosely coupled temperatures (translational and rotational) and thus two separate thermostats. In our previous work [8] we have analysed the effect of Nosé-Hoover thermostat parameters in terms of system's ergodicity and potential errors in chemical potential profiles. Tight thermostating resulted in a non-ergodic system with the chemical potential shifted by about 0.8 kJ/mole (the corresponding change in potential energy was much less pronounced). And while overly 'loose' thermostats will ultimately yield correct results in the case of an NVT ensemble the long-term fluctuations in potential energy might affect the grand canonical number dynamics in an unpredictable way.

Coupled equations (1-12), already containing quarternions and 'friction' coefficients, are complicated still further by grand-canonical variable,  $\zeta(t)$ , the degree of presence of the fractional particle. To solve the equation set we have modified the implicit quarternion scheme of [16] for a thermostat formulation [18]. Time step was 0.5 fs, with the reasons for choosing such short a timestep outlined elsewhere [8].



## 4. RESULTS AND DISCUSSION

Figures 1 and 2 show the results of applying the grand canonical molecular dynamics scheme of [10-12] modified for Nose-Hoover thermostat [14,15] to simulation of model water system driven by different chemical potentials. A  $\mu VT$  ensemble of rigid TIP4P water molecules [19] was investigated at 298K. Under standard conditions our periodic cell should contain 108 water molecules corresponding to the density of  $0.998 \text{ g/cm}^3$ . As it could also be seen from figure 1, for quite a long time following the equilibration period both single-particle systems seemed to reach a steady state. Note that the chemical potential-density curve (increase in chemical potential bring the decrease in density) on this plateau agreed with the findings of both thermodynamic integration and GCMD [12,20]. But then the number of molecules in the system held at  $\mu=-23.00 \text{ kJ/mol}$  went up from 107 to 115 and so far appears to stay there. This behaviour can be compared to the time history in figure 2 of [11] where a system holding steady at about 132 LJ particles for 200 ps suddenly climbed up by almost 10 particles and then went down to about 135 particles. This pattern may reflect the inherent tendency of the present grand canonical MD scheme to freeze in metastable states. It also becomes apparent from figure 1 that no driving chemical potential reasonably close to the real-life one was able to reproduce the actual density of water.

It was our belief that this failure could be linked to the inadequacy of a single fractional particle as chemical potential ‘probe’. Feeling the need for a more robust and responsive approach we have extended the treatment of Pettitt and co-workers to introduce multiple fractional particles. Figure 2 shows the number of particles dynamics for a system with four fractional particles, with the time evolution of each one governed by its own eq. 12.

Just as in the case of a single fractional particle, only full particles are counted when the ‘number of particles’ is considered. A closer look at eq. 12 shows that the number acceleration of the just created particle (with an almost-zero fraction) can be highly negative, which raises doubts whether the scheme will ever allow the particle to survive after creation. With this concern in mind we should draw the reader’s attention to the curve of figure 2 corresponding to  $\mu_{\text{ex}} = -22.40$  kJ/mol (Curve 3), it demonstrates that the system can generate particles at a runaway rate when driven to do so by external chemical potential. Curve 2 of figure 2 shows that when the initial density does not match the desired chemical potential the system’s response is first to ‘exacerbate’ the situation during the early stages of its equilibration. This response seems to be shared by constant- $\mu$  systems simulated by Pettitt and co-workers.

Exploring the range of chemical potential we have discovered a rather sharp ‘cut-off’ to the left of its physical value at 298 K. When the driving chemical potential is set below -24.3 kJ/mol, sooner or later the system undergoes a downward density fluctuation from which it never recovers (see the plunge in figure 3). This behaviour could be compared to that of Curve 2 in figure 2, one could see that systems at  $\mu_{\text{ex}} = -23.50$  and  $-24.00$  kJ/mol did bounce back from fluctuations comparable in absolute depth. In our opinion the difference lies in the fact that though quite dramatic, the downward fluctuations at higher potentials never result in overall densities that could lead to non-uniform changes in local densities described in [21] (compare figure 3 (a) and (b) of this ref.). When confronted with the cavitation effect, present insertion scheme will allow the new particle to be created at the outskirts of high-density regions rather than in the middle of empty ones, and the new particle will probably never survive the vaporisation.

Average potential energies of the two ‘4-particle’ systems were calculated by averaging over interactions of both full and fractional particles. We should note that the difference in potential energies was consistent but small (about 0.25 kJ/mole). And since the difference is much less than that between the driving chemical potentials, it underlines even further the importance of entropy contribution and thus raises the whole issue of system’s ergodicity [8].

Furthermore, we have found that the slope of potential energy-density curve is not steep in the 90 through 120 particles interval. Consider figure 4 showing the per-particle potential energy and the number of particles less their respective run-time averages. In general, though the Coulomb contributions to the net potential energy clearly dominate ( $-4812$  kJ/mol versus  $+796$  kJ/mol in terms of total potential energy), particle fluctuations are in a counterphase with the energy, a behaviour expected from a purely Lennard-Jones system to the right of energy minimum. This fact could also explain that though not totally conclusive at this point, our findings agree with those of [12,20] in the part that the increase in chemical potential resulted in the decrease of density. The lowest of stable chemical potentials,  $-24.2$  kJ/mole, corresponded to the highest density, while  $\mu_{\text{ex}} = -22.9$  kJ/mol resulted in density slightly lower than the physical one.

The applicability of developed four-particle scheme has been tested further on a methanol system with 3-site potential from [22] at 298K and density  $0.786 \text{ g/cm}^3$  (see Figure 5 for potential energy) . Figure 6 presents density fluctuations at three different driving chemical potentials. Curve *a* corresponds to chemical potential for the model employed ( $-19.0$  kJ/mol, estimated by us through thermodynamic integration); curves *b* and *c* test the system’s sensitivity to chemical potential deviations. One can see that

while density of systems  $c$  and  $b$  has responded to non-physical at chemical potentials by going, respectively, up and down, system  $a$  appears to be holding steady at nearly physical density.

## 5. CONCLUSION

Our modification of the grand canonical molecular dynamics of Pettitt and co-workers [10-12] enables a constant-temperature dynamics with multiple Nosé-Hoover thermostats. As such, it opens the possibility of using quaternion treatment for rigid molecules (with translational and rotational temperatures controlled by separate thermostats) rather than limiting the choice to SHAKE/RATTLE-like algorithms.

The results for single fractional particle show slow equilibration and a tendency of the system to get stuck in metastable states for long periods of time, traits apparently shared by constant- $\mu$  systems simulated by Pettitt and co-workers [see fig. 2 of ref.11]. We concluded that though a single fractional particle may be suitable for calculation of chemical potential in homogenous systems, its extremely slow and uncertain response makes it a poor candidate for implementation of multicomponent interfacial systems.

Our ongoing investigation into an open system featuring four fractional particles shows much more promise. The equilibration period is shorter and the number of particles appears to be more stable and not prone to freezing in metastable configurations. The feasibility of the scheme is confirmed further by investigating an open methanol system. It is our belief that a ‘four-particle’ scheme could be used to control chemical potential for both homogenous and interfacial systems.

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## FIGURE CAPTIONS

Figure 1. Number of full particles for several driving chemical potentials in case of a single fractional particle (TIP4P water).

Figure 2. Number of full particles in case of 4 fractional particles (TIP4P water).

Figure 3. Number fluctuation leading to the system breakdown in case of  $\mu_{\text{ex}} = -25.00 \text{ kJ/mol}$  (TIP4P water).

Figure 4. Fluctuations in potential energy and the number of particles for  $\mu_{\text{ex}} = -24.00 \text{ kJ/mol}$  (TIP4P water).

Figure 5. Methanol potential energy vs. inverse temperature at  $\rho = 0.786 \text{ cm/cm}^3$ .

Figure 6. Number of full particles for three different chemical potentials, methanol system at 298 K. Straight line is experimental density.













